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BRIEF COMMUNICATIONS

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IRREVERSIBLE CATALYSIS OF CYCLOHEXENE ON ACTIVATED CARBON OF A HIGH DEGREE OF PURITY

The reaction of hydrogen redistribution within the molecule of organic compounds, which was studied by one of us and Glinka (1) back in 1911, was subjected during subsequent years to extensive investigations. In this connection the following were studied: the transformations on contact with platinized and palladinized carbon (as well as with other catalysts) of hydrocarbons of the cyclohexene and cyclohexadiene series, of terpenes, and of some other incompletely hydrogenated ring systems. Until recently, however, it had not been ascertained whether pure activated carbon (i.e., elemental carbon) is adapted for use as a catalyst in the irreversible catalysis reaction.

It is known that activated carbon possesses inherent catalytic properties, a fact which is attested to by the fairly large number of papers and a still greater number of patents disclosing the catalytic activity of carbon in reactions of polymerization, condensation, halogenation, hydrohalogenation, dehalogenation, reduction, axidation, and also in some cases of isomerization and dehydrogenation. Use of carbon in hydrogenation reactions has also been disclosed, but in this instance data found in the literature are most contradictory and make it necessary to assume that the hydrogenation of hydrocarbons (and possibly also some of the

other above-enumerated reactions) occurs only on using carbons with a high ash content, wherein the iron, copper, zinc, and other elements present in the form of admixtures may display an inherent catalytic effect or act as promoters (2).

Among the numerous publications devoted to the study of catalytic properties of carbon there is but a single one by Rudakov and co-workers (3) in which was studied the irreversible catalysis (and dehydrogenation) of dipentone and Δ_3-carene in the presence of carbon. These authors utilized as a catalyst activated birch charcoal, the ash content of which is usually rather high. In the course of this work it was established that at 400 to 500 degrees Centigrade irreversible catalysis of the above-mentioned hydrocarbons occurs, while on further increase of the temperature dehydrogenation begins (with an optimum at 550 to 600 degrees Centigrade). The authors of the publication have found that either of these reactions (especially that of dehydrogenation) does not proceed smoothly but is accompanied by secondary reactions of isomerization and thermal decomposition.

We have studied the irreversible catalysis reaction of cyclohexene in the presence of carbon obtained by carbonization of recrystallized sugar and subsequent activation in a current of carbon dioxide. The carbon thus prepared had an activity of ether: 10 percent per hour, 42 percent over 24 hours. The ash content of this carbon was negligible -- a spectral analysis revealed only traces of iron (of the order of 0.01 percent) and the absence of any other admixtures.

Experimental Procedure

The cyclohexan used in the experiments was carefully purified and had the following constants: boiling point 82.5 degrees Centigrade at 757 millimeters pressure; n_D^{20} 1, 4460; d_D^{20} 0.8100; formed MR_D 27.11, calculated for C_6H_{10} MR_D 27.24.

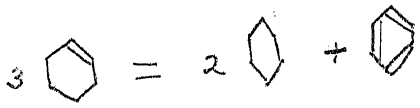
The investigation was conducted using the conventional apparatus for experiments utilizing the continuous current method. Special care was taken to maintain constant temperature and rate of feed of starting materials during the entire time of the the experiment, and also to ensure high purity of the hydrogen and efficient cooling of the receiver. Material of the reactor made of pyrex glass did not display any catalytic properties in the reactions studied. Analysis of the catalysate for cyclohexene content was conducted using the method of bromometric titration with concurrently conducted control experiments and recording of combination light scattering spectrum, as well as conducting qualitative colorimetric reactions for the detection of benzene (using an ammonia solution of potassium cyanide). To confirm the absence under the hereinafter described conditions of any hydrogenating properties of the carbon used as the catalyst, experiments were conducted with α-nonene. As a result of these experiments it was demonstrated that at 400 to 450 degrees Centigrade α - nonene does not undergo hydrogenation in the presence of an excess of hydrogen. The results obtained are shown in the composite table given below.

Starting materials	Temperature of the experiment in °C	Space velocity of liquid fed	n_D^{20} OF starting material	n_D^{20} of catalyzate	Percentage of conversion by titration	Qualitative reaction for benzene
Cyclohexene in the absence of hydrogen sen	400	0.6	1.4460	1.4469	12.5	Positive
Cyclohexene in the absence of hydrogen	450	0.6	1.4460	1.4472	29.5	Positive
Cyclohexene in the absence of hydrogen	475	0.6	1.4460	1.4470	26.1	Positive
Cyclohexene in an excess of hydrogen	400-450	0.6	1.4460	1.4461	0.7	Negative
α-nonene in an excess of hydrogen	400-450	0.6	1.4148	1.4151	0.4	Negative

The presence in the catalyzate of benzene and cyclohexane in a definite ratio was determined by recording the spectrum of combined light scattering. According to the spectrographic data the catalyzate obtained on passing cyclohexane over the carbon in the absence of hydrogen at 450 degrees consisted of 64 percent cyclohexane, 24 percent cyclohexane, and 12 percent benzene (no traces of five-numbered ring hydrocarbons were detected).

Conclusion

1. Irreversible catalysis of cyclohexene over carbon begins at a temperature of approximately 400 degrees and reaches a maximum at 450 degrees. At 450 degrees, and in the absence of hydrogen, cyclohexene (with a space velocity of 0.6 milliliters per milliliter of catalyst per hour) readily undergoes transformation in accordance with the equation:



In an excess of hydrogen at 400 to 450 degrees an irreversible catalysis of cyclohexene in the presence of carbon practically does not take place.

2. Hydrogenation of cyclohexene with an excess of hydrogen and in the presence of the carbon utilized in our experiments does not occur at 400 to 450 degrees.

3. Thus in the present work we have extended the reaction of irreversible catalysis of cyclohexene to the case wherein there

is used as catalyst activated carbon of a high degree of purity prepared by carbonization of sugar.

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